M E M O R A N D U M

TO: File

FROM: Tom Smythe
Water Resources Engineer

SUBJECT: Sediment Phosphorus and Nitrogen Monitoring and Trends

DATE: April 25, 2016

Lakebed Management funds collection and analysis of sediment cores in Clear Lake to document the internal phosphorus loading. Sediment cores were collected beginning in 1995 to follow up on some hypotheses in the Clean Lakes Report[1]. The Report hypothesized that the Clear Lake ecosystem moved from being dominated by external loading in the 1960's and early 1970's to being dominated by internal loading during the early 1990's. Verification and quantification of phosphorus cycling from the sediments required measurement of phosphorus concentrations in the lake sediment.

A 25 cm core was collected in the Upper Arm and Ekman dredge samples were collected in the Lower and Oaks Arms. Based on an evaluation of the data to date[2], the sampling program was modified in 1998 and 10 cm cores were collected in all three Arms. Originally, sediment samples were collected by County staff concurrent with water quality data, however, to improve the efficiency of both operations, the County and California Department of Water Resources (CDWR) agreed in 1999 that the County would provide the use of a boat to CDWR in exchange for additional monitoring and collection of the sediment samples by CDWR.

Phosphorus

Sediment was analyzed for phosphorus in various forms[3] by the Hopland Research and Extension Center, University of California through 2007. Beginning in 2008, samples were analyzed using the same procedure by the Tahoe Environmental Research Center Laboratory, University of California-Davis.

Data collected from the sediment cores has not been analyzed by limnologists/microbiologists since the 1997 work of Richerson et al.[1]. Due to questions raised by the Board of Supervisors in 2010, I conducted analyses using similar techniques to those of Richerson. This report analyzes Data collected through September 2015.

---

[1] Richerson, Peter J., Suchanek, Thomas H., Why, Stephen J., The Causes and Control of Algal Blooms in Clear Lake, Clean Lakes Diagnostic/Feasibility Study for Clear Lake, California, prepared for Lake County Flood Control and Water Conservation District, 1994

[2] Richerson, P. J., Stauffacher, K., Suchanek, T. H., Vaughn, C.E., Thibeau, D., Why, S. J., "The Phosphorus Cycle in an Iron Limited Lake", First Annual Clear Lake Science and Management Symposium Proceedings Volume, 1997

[3] Hieltjes, Arnold H. M., Lijklema, Lambertus, "Fractionation of Inorganic Phosphates in Calcareous Sediments**",** Contribution of the Dept. of Chemical Engineering, Twente Univ. of Technology, P.O. Box 217, Enschede, The Netherlands. Received 19 Nov. 1979

The data indicated that:

- Phosphorus cycling is continuing to occur in the top 10 cm of the sediment.
- Total phosphorus concentrations and mass, as well as the solids content were declining in the top 10 cm of the sediment.
- Based on sediment cores up to 3 meters in length[4], this appears to indicate that the lake sediments were trending towards the pre-European conditions.

Based on these analyses, I make the following observations:

- Total Phosphorus: Data was analyzed for the common period of August 1997 through September 2015. The total phosphorus concentration was averaged for the entire 10 cm core. Data trend lines were inserted utilizing Microsoft Excel, see attached charts. All three arms of the lake show a decrease in total phosphorus concentrations of 3.9 to 10 µg/g/yr[5]. Decreases in phosphorus mass are further magnified by the increase in water content of the sediments. Phosphorus mass is decreasing 4.9 to 38 T/yr in each Arm, with a total decrease of 53 T/yr in the entire lake. Trends for total phosphorus are listed below[6]:

		Change in Total P Concentration, µg/g/yr	Change in Total P Mass, T/yr[7]	Change in Percent Water, %/yr
CL1	Upper Arm	-3.9	-35	0.16
CL3	Lower Arm	-9.0	-10	0.086
CL4	Oaks Arm	-14	-4.6	0.14
	Clear Lake		-50	

  This decrease is encouraging, as it appears to show a decrease in external total phosphorus loading and a potential decrease in phosphorus available for internal phosphorus cycling/loading. This decrease in phosphorus is thirty two to fifty six percent (34-56%) of the external loading (Richerson, 1994[1], 158 T P/yr; LCWPD, 2009[8], 90-125 T P/yr.

  Unfortunately, the amount of phosphorus cycled from the sediments remains in excess of 500 T each year, over five times the average annual phosphorus load.

- Calcium Bound Phosphorus: This component of sediment phosphorus is tightly bound and does not appear to be readily released to the water column. Calcium bound phosphorus was analyzed in a similar manner to Total Phosphorus. Calcium bound phosphorus concentrations are increasing in all three Arms, ranging from 3.9 to 8.1 µg/g/yr. The mass of

---

[4] Richerson, Peter J., Thomas H. Suchanek, Robert A. Zierenberg, David A. Osleger, Alan C. Heyvaert, Darell G. Slotten, Collin A. Eagles-Smith, and Charles E. Vaughn, "Anthropogenic Stressors and Changes in the Clear Lake Ecosystem Recorded in Sediment Cores," Ecological Applications, 18(8) Supplement, 2008, pp. A257–A283

[5] Note: In the regression equations, "x" is number of days.

[6] Negative numbers indicate a decreasing value with time.

[7] Regressions were calculated for each Arm and the Lake independently, therefore, the totals from all three arms may not total the Lake change.

[8] Lake County Watershed Protection District, Final Report, Clear Lake Watershed TMDL Monitoring Program, April 14, 2009

this relatively inert form of phosphorus is increasing in the Upper and Lower Arms, while staying constant on the Oaks Arm. Trends for calcium bound phosphorus are listed below:

		Change in Ca P Concentration, µg/g/yr	Change in Ca P Mass, T/yr	Change in Percent Water, %/yr
CL1	Upper Arm	4.3	0.68	0.16
CL3	Lower Arm	8.1	1.5	0.0.86
CL4	Oaks Arm	3.9	-0.13	0.14
	Clear Lake		0.84	

The overall increase in the relatively inert calcium bound phosphorus mass, combined with the decrease in total phosphorus mass, indicates the phosphorus mass in the sediments in Clear Lake is becoming more inert, reducing the quantity of phosphorus available for phosphorus cycling into the water column.

- Iron and Aluminum Bound Phosphorus: This component of sediment phosphorus is loosely bound and can readily enter the water column. Iron and aluminum bound phosphorus was analyzed similar to total phosphorus. The concentrations do not appear to be changing significantly over time, increasing by up to 0.8 µg/g/yr. When coupled with the increased water content, the mass of loosely bound phosphorus is decreasing slightly in the lake (8.2 T/yr). Trends for iron and aluminum bound phosphorus are listed below:

		Change in Total Fe-Al P Concentration, µg/g/yr	Change in Fe-Al P Mass, T/yr	Change in Percent Water, %/yr
CL1	Upper Arm	0.82	-4.3	0.16
CL3	Lower Arm	-2.6	-3.3	0.086
CL4	Oaks Arm[9]	-2.5	-1.2	0.14
	Clear Lake		-8.2	

While two Arms show an overall increase in phosphorus concentration, due to the increased sediment water content, the mass of phosphorus is decreasing lakewide.

- Comparison to pre-European phosphorus concentrations: We estimated pre-1927/pre-European concentrations of the various phosphorus fractions in the 3 meter sediment cores from Figures 11 and 12 from Richerson[1]. Data was not included in the report, so the average concentrations were visually estimated. These concentrations are considered “target concentrations” for returning Clear Lake to its pre-European condition. These estimates are shown below along with the September 22, 2015 average concentrations calculated from the trend lines noted above.

[9] The last few years, the analysis showed this was increasing. It isn’t clear at this time whether the concentration is starting to decrease of this is a result of sampling “noise”. Any change is negligible as the average concentration is nearly 500 µg/l in the Oaks Arm.

With the exception of the Total Phosphorus in the Upper Arm, phosphorus concentrations are still significantly above the pre-European concentrations, with the greatest discrepancy in the readily available iron and aluminum bound phosphorus. In all cases, the greatest difference between current and target phosphorus concentrations are in the Lower and Oaks Arms. Utilizing the current rate of change from the trend lines, we calculated the number of years it would take to reach the target concentration for each Arm and phosphorus form.

As the Upper Arm sediments are primarily inorganic sediments deposited by the streams draining the watershed (approximately 85% of the surface water and sediment entering Clear Lake enters in the Upper Arm) and the total phosphorus concentration is essentially equal to the target (pre-1927) total phosphorus concentration, this indicates that the primary source of total phosphorus in the Upper Arm is sediment. There do not appear to be significant additional sources of total phosphorus to the Upper Arm.

Analyte	Arm	Station	July 1, 1998 Conc, ug/g	Sept 22, 2015 conc, ug/g	Pre-1927 Target Conc, ug/g	Ratio 2015/Target	Years	Years to Target at Current Rate
Total P	Upper Arm	CL1	1,252	1185	1270	93.3%	21.5	Diverging
Total P	Lower Arm	CL3	1,799	1644	800	205.5%	-92.7	93
Total P	Oaks Arm	CL4	1,703	1458	707	206.2%	-52.0	52
Ca P	Upper Arm	CL1	290	364	311	117.0%	12.1	Diverging
Ca P	Lower Arm	CL3	336	475	300	158.5%	21.3	Diverging
Ca P	Oaks Arm	CL4	305	373	308	121.0%	16.2	Diverging
Fe-Al P	Upper Arm	CL1	280	294	86	342.0%	249.9	Diverging
Fe-Al P	Lower Arm	CL3	599	554	102	542.7%	-168.3	168
Fe-Al P	Oaks Arm	CL4	495	451	114	395.8%	-131.1	131
Resid P	Upper Arm	CL1	683	527	873	60.3%	37.8	Diverging
Resid P	Lower Arm	CL3	864	615	398	154.6%	-14.8	15
Resid P	Oaks Arm	CL4	903	634	285	222.3%	-22.0	22

The sediments in the Lower and Oaks Arms have more than twice the total phosphorus concentration than the target concentration. The sediments in these Arms are significantly enriched. With little surface inflow in these Arms, sediments consist of very fine inorganic and organic particles carried from the Upper Arm by currents and deposition of organic material (algae and cyanobacteria) which grow within the Arms. As some of the most prolific algal and cyanobacteria growth occur in these two Arms, this is a self feeding cycle, however, concentrations are gradually decreasing. We note that if total phosphorus levels continue decreasing at the current rate, it will take 93 and 52 years for the Lower and Oaks Arms, respectively, to reach the target concentration. Additional changes to the lake ecosystem, such as major wetland restoration, could change this time period significantly.

Calcium bound phosphorus concentrations are higher than the target concentrations and are continuing to increase, however, as calcium bound phosphorus is tightly bound and not readily available for cycling, this is actually beneficial.

The iron and aluminum bound phosphorus concentrations are significantly higher than the target levels, with the Upper Arm showing a slight increase over time. The Lower and Oaks Arms are currently showing decreases. In all cases, the change is minimal (<10% change over 17 years) and may not reflect actual changes. The biggest issue is that the readily available phosphorus is 3.4 to 5.4 times the natural concentrations. Since this is the most readily available phosphorus for cycling into the water column, these highly elevated concentrations are not encouraging. It is not clear why the iron and aluminum bound phosphorus are elevated to a greater extent than other forms, although it may due to sediment chemistry changes caused by increased sulfate loading as hypothesized by Richerson et al., 2008[3].

Detailed analysis of Clear Lake's sediment chemistry and nutrient cycling is necessary to understand the driving factors in phosphorus cycling, why the "balance" of phosphorus types is skewed towards readily available phosphorus and what measures, if any, can be taken to reduce phosphorus cycling to near natural levels.

Nitrogen

In 2011, we became aware of a study in Upper Klamath Lake where nitrogen cycling was determined to be a significant source of nitrogen for cyanobacteria. Utilizing the ammonium flux rates from Upper Klamath Lake, 50 – 1,300 T/yr of ammonium could be cycled into the water column from the sediments. In comparison, the estimated annual nitrogen load from the watershed is estimated to be 273 – 379 T/yr. Therefore, starting in December 2011, the 10 cm sediment cores were analyzed for nitrogen content in addition to phosphorus content. While very preliminary, following is an analysis of the December 2011 through September 2015 nitrogen data:

- Nitrogen was analyzed from the pore water in the sediments. Nitrogen analyses were broken down into the following types:
  - Total Kjeldahl Nitrogen (TKN): TKN consists of ammonia, ammonium and organic nitrogen.
  - Nitrate plus nitrites
  - Total nitrogen: This is the sum of the two types of nitrogen listed above.
- Nitrogen concentrations change throughout the year. The pattern of high sediment nitrogen during the winter months and low sediment summer nitrogen levels is similar to the pattern exhibited by sediment phosphorus. The nitrogen in the sediment probably comes from

decaying organic matter, such as fish, green algae and cyanobacteria, as they die and sink to the bottom as the summer and fall progresses. Nitrogen levels in the sediment decrease in the spring, reaching a low in the early summer. If this nitrogen reenters the water column and is utilized by green algae and cyanobacteria, it would be a significant nitrogen source for the lake ecosystem.

- The changes in nitrogen concentrations are more pronounced in the upper portion of the sediments, and may cycle from sediments deeper than 10 cm. Additional data is necessary to confirm depth of cycling. It is possible that the nitrogen is more mobile than phosphorus as nitrogen is primarily within the pore water, and phosphorus is primarily attached to the sediment particles.
- As sediment nitrogen concentrations change, it is assumed the nitrogen moves in and out of the water column. Based on the first few years of data, sediments could contribute over 500 metric tons of nitrogen to the water column during the growing season. This is significant, as we have estimated the average annual inflow of nitrogen is 273 to 379 metric tons per year[8] and the total nitrogen budget for Clear Lake was estimated to be 1,100 T per year by Horne[10]. Horne assumed the majority of the nitrogen in the lake was from nitrogen fixation by some cyanobacteria. Review of the CDWR data through 2012 confirms the nitrogen budget remains near 1,100 T/yr. These numbers indicate sediment nitrogen carried through the winter may be one of the largest sources of nitrogen for the Clear Lake ecosystem each growing season.

The preliminary data appears to indicate sediment nitrogen could play a significant role in algal and cyanobacteria productivity in Clear Lake. Additional sampling is necessary to confirm these preliminary findings.

Conclusion

Sediment sampling to date has confirmed that nutrient cycling from the lake sediments is a major source of nutrients for the Clear Lake ecosystem. We make the following findings:

- Phosphorus concentrations in the sediments are elevated above target (pre-1927) concentrations, which contribute to internal phosphorus cycling in Clear Lake. The greatest increases in phosphorus concentrations are in the Lower and Oaks Arms.
- Total phosphorus concentrations and mass in Clear Lake sediments are decreasing at a rate of approximately 50 T per year since 1997, an indication that external phosphorus loading has been decreased significantly. This decrease is probably due to a reduction in external phosphorus loading from historical levels.
- Calcium bound phosphorus is increasing, further reducing the mass of phosphorus available for internal cycling.
- Concentrations of readily available iron and aluminum bound phosphorus are increasing. The cause is unknown and needs to be evaluated by someone with better understanding of sediment chemistry and nutrient cycling.
- Detailed analysis of Clear Lake's sediment chemistry and phosphorus cycling is necessary to

[10] Horne, A. J. , Dr., Clear Lake Algal Research unit, First Annual Report (1969-70), Nitrogen Fixation, Related Parameters and their Effects on Blue-green Algal Blooms, Report to Supporting Organizations, June 1971

understand this very large source of phosphorus during the growing season. Mitigation of and reduction of phosphorus cycling could be developed when the system is better understood.

- With only four years of data, little can be deduced from the nitrogen data at this time. More years of data are necessary to confirm these preliminary findings.
- The depth of nitrogen cycling cannot be verified, however, it appears nitrogen cycling is confined to the top 10 centimeters of the core, and possibly the top 6 centimeters.
- There may be in excess of 500 T of nitrogen cycled from the lake in the summer, to the sediment in the fall-winter, then back into the lake the next summer. This could be the largest source of nitrogen available to the algae and cyanobacteria during the growing season.
- There is insufficient data to determine if there is an increasing or decreasing trend with nitrogen in the sediment.
- Detailed analysis of Clear Lake's sediment chemistry and nitrogen cycling (if it is actually occurring) is necessary to understand this potentially large source of nitrogen during the growing season. Mitigation of and reduction of n itrogen cycling could be developed when the system is better understood.

The internal nutrient loading that is occurring with phosphorus and nitrogen cycling through the sediments (winter) and water column (summer) appears to be the greatest source of nutrients to green algae and cyanobacteria in Clear Lake. External phosphorus loading has been significantly reduced, however, the internal nutrient loading is continuing to support excessive growth of cyanobacteria. Understanding this nutrient cycling is necessary in order to develop measures to improve summer conditions in Clear Lake. This understanding is facilitated by possession of a substantial data set. The sediment nutrient dataset compliments the water quality dataset that has been collected by CDWR.

We leave you with a 1975 quote by Dr. Alex Horne, one of the early researchers on Clear Lake:

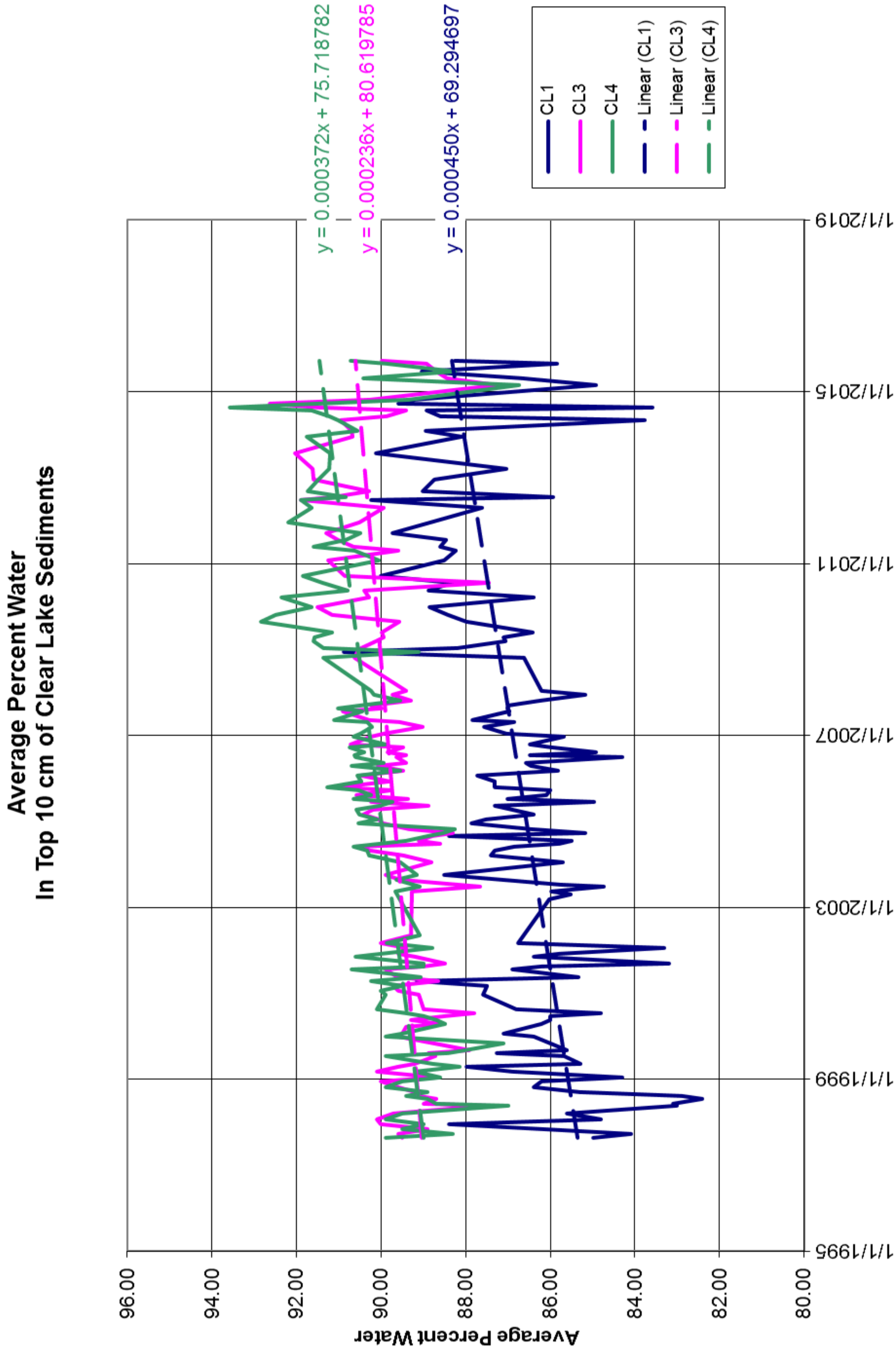
> The main purpose of CLARU's activities from 1970-74 has been to carry out research to determine precisely how and why algae, particularly blue-green algae, follow daily and seasonal patterns which sometimes give rise to severe nuisance conditions on Clear Lake. From the outset it was realized that this was a complex problem not amenable to a study involving occasional lake measurements, some chemical analysis and judicious use of the literature. There are many lakes throughout the world with nuisance blue-green algae and their ecologically sound, economical management is not routine by any stretch of the imagination.[11]

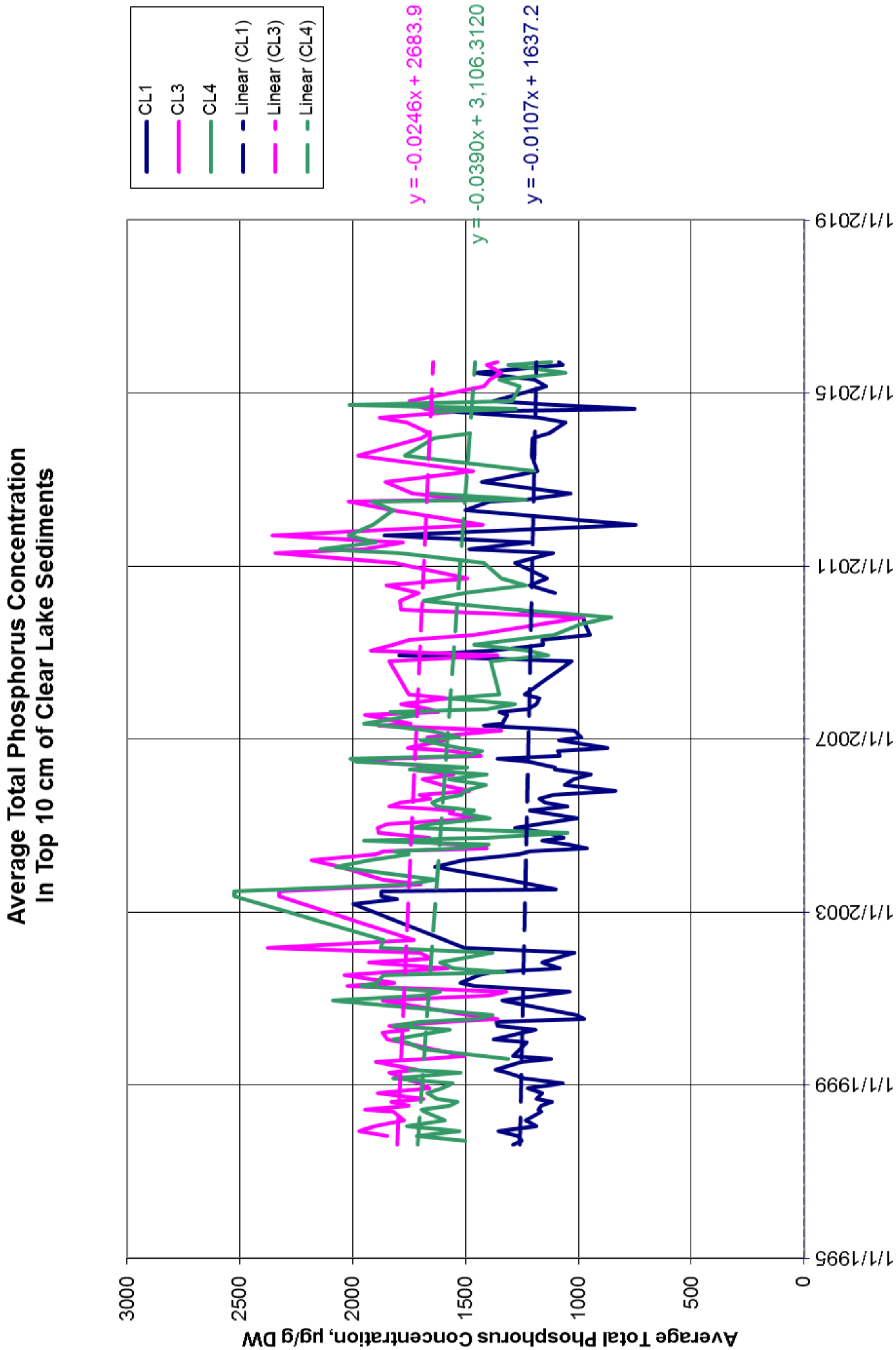
If you have any questions, please contact me.

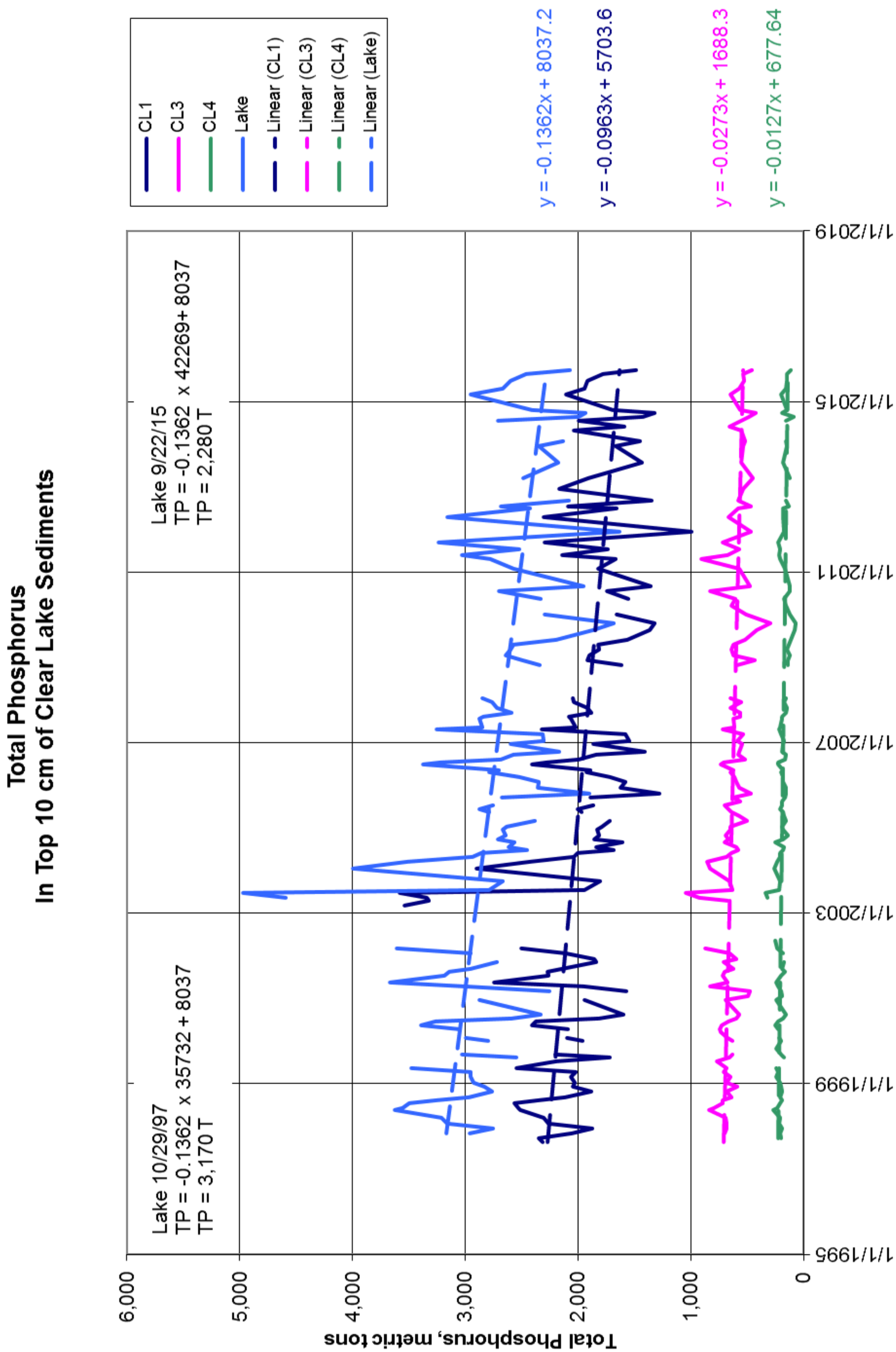
TRS:trs

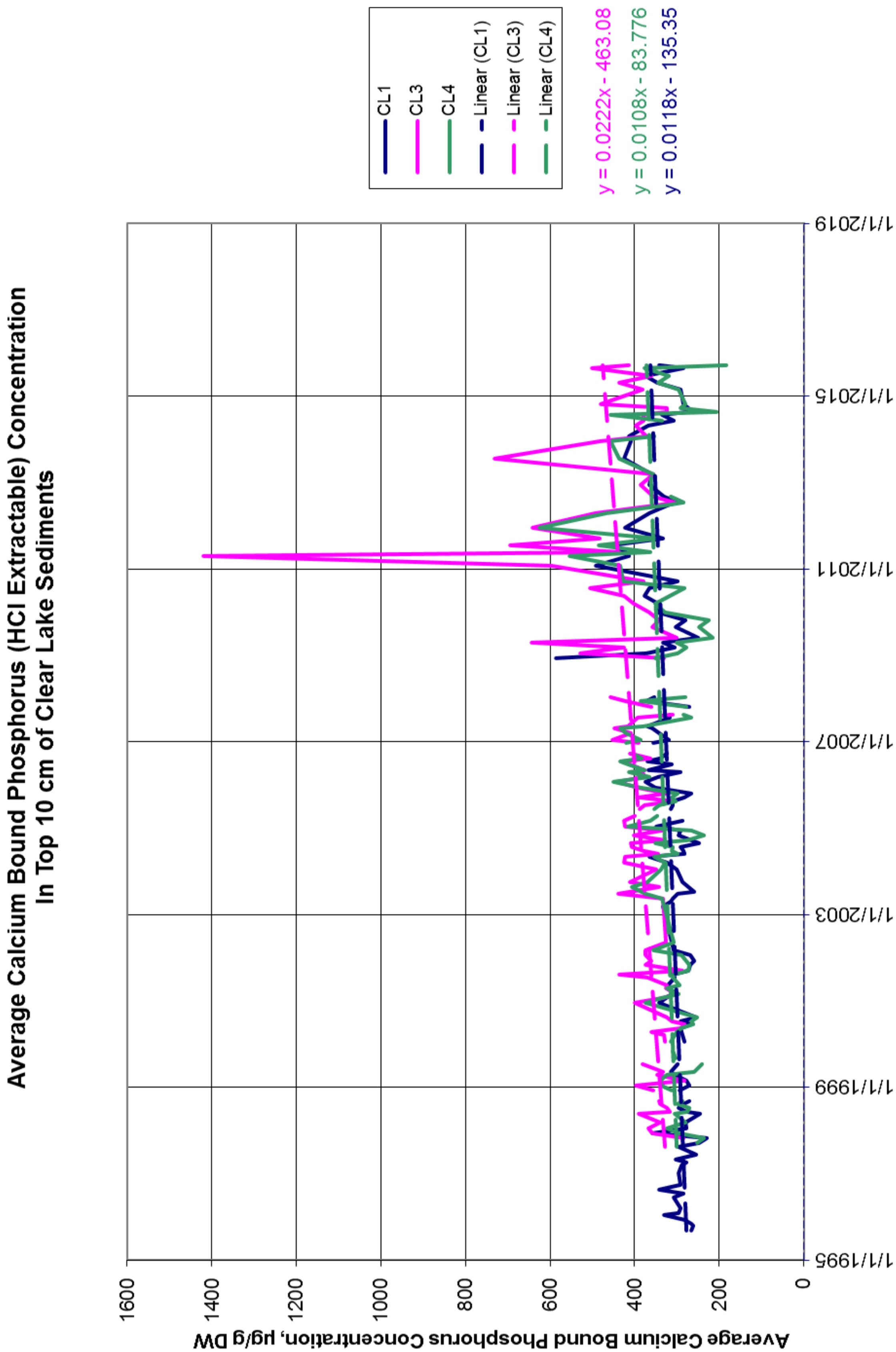
W:\Water Quality Data\Sediment Cores\Trend Analysis.doc

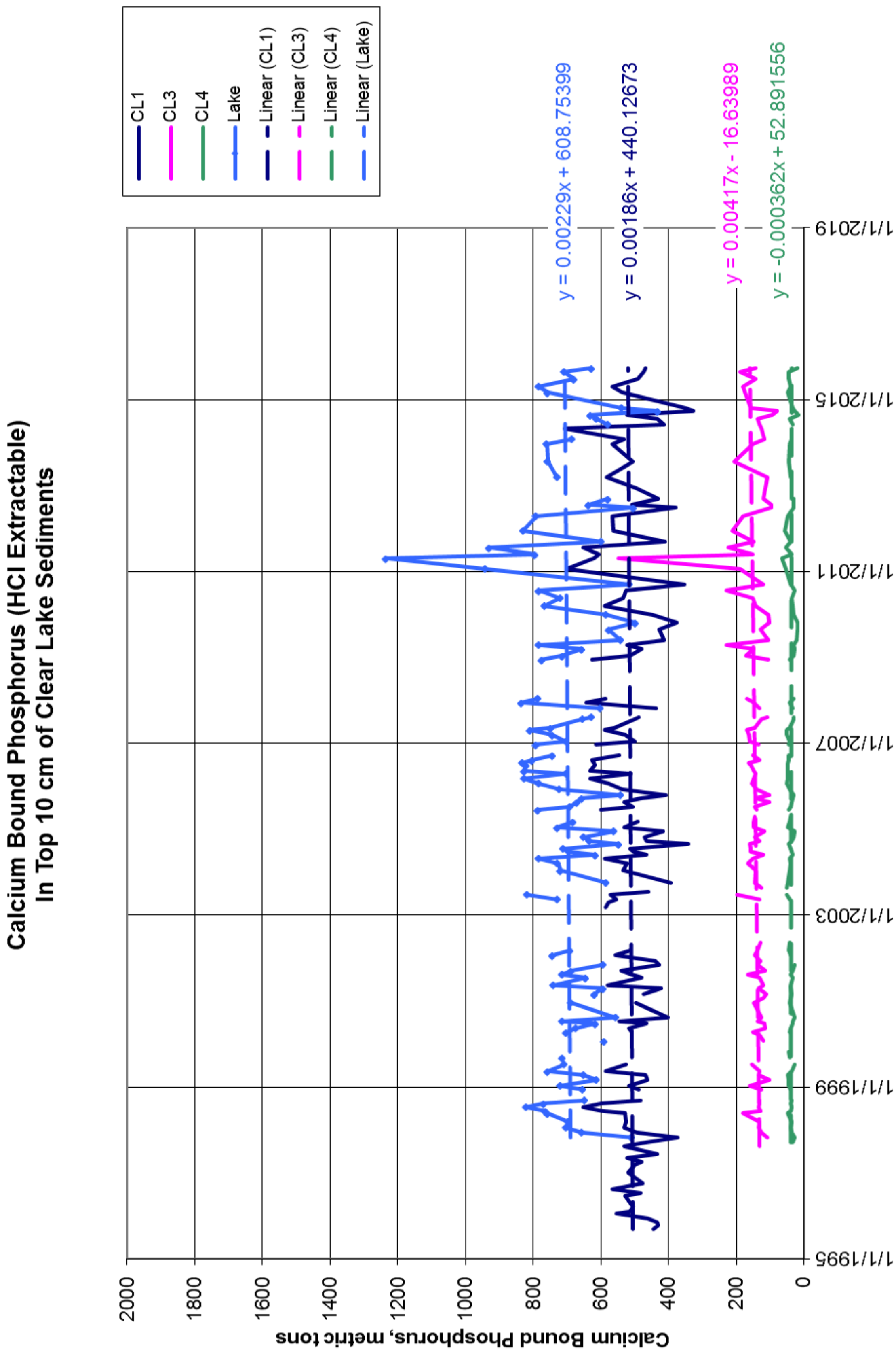
[11] Horne, A. J., The Ecology of Clear Lake Phytoplankton, Clear Lake Algal Research Unit, 1975

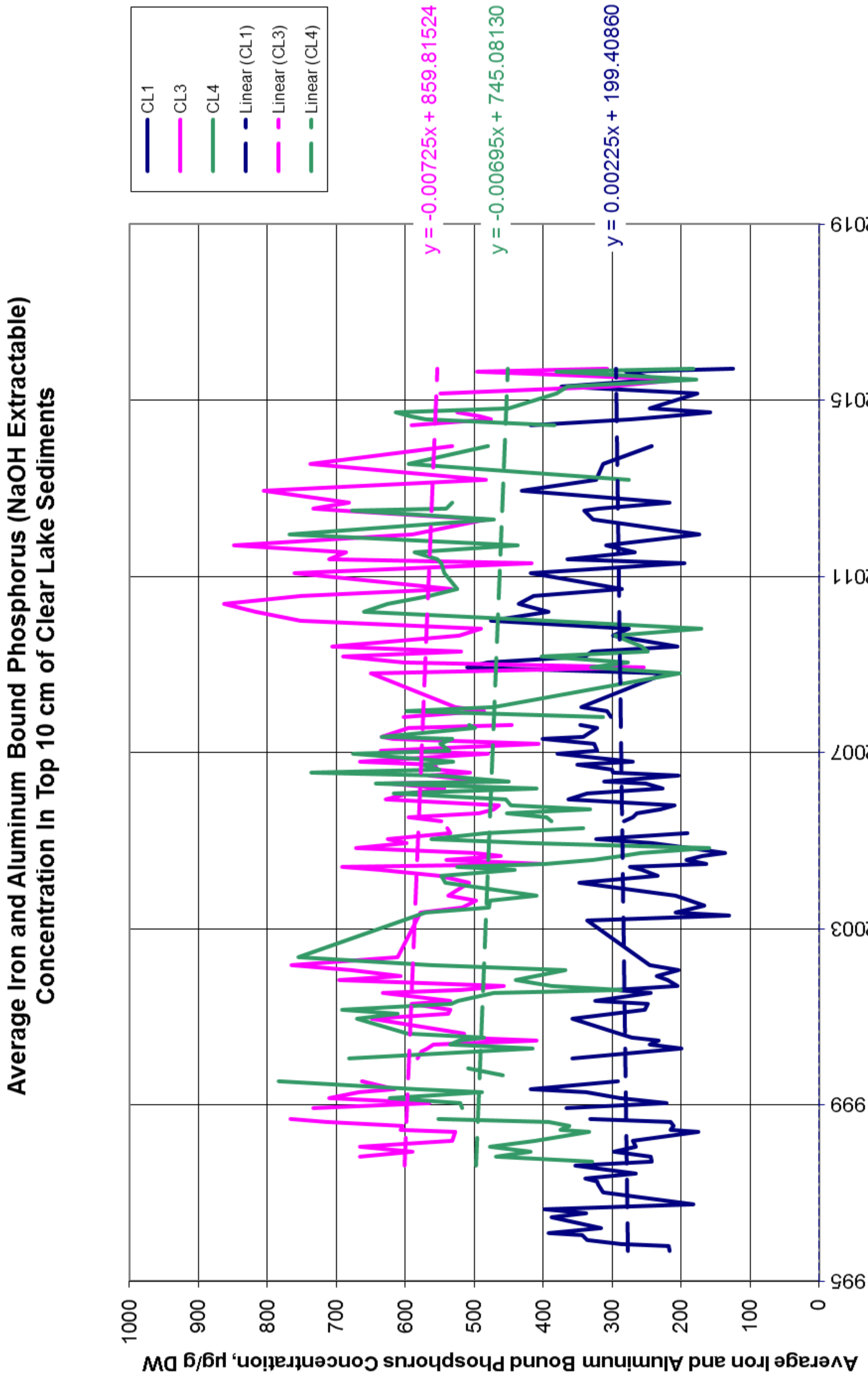

Average Percent Water
In Top 10 cm of Clear Lake Sediments
y = 0.000372x + 75.718782
y = 0.000236x + 80.619785
y = 0.000450x + 69.294697
CL1
CL3
CL4
Linear (CL1)
Linear (CL3)
Linear (CL4)
Average Percent Water
96.00
94.00
92.00
90.00
88.00
86.00
84.00
82.00
80.00
1/1/1995
1/1/1999
1/1/2003
1/1/2007
1/1/2011
1/1/2015
1/1/2019

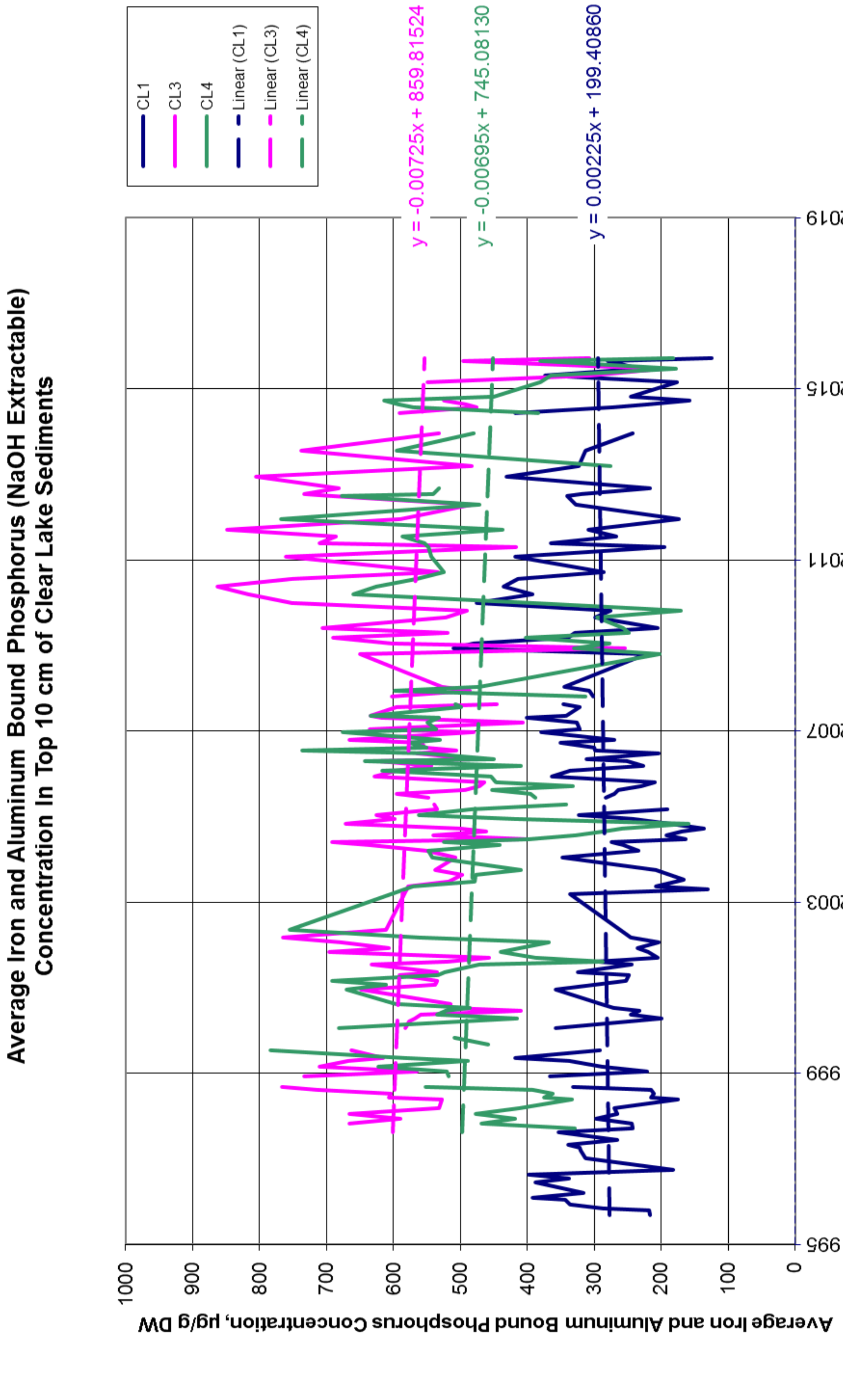

Average Total Phosphorus Concentration
In Top 10 cm of Clear Lake Sediments
CL1
CL3
CL4
Linear (CL1)
Linear (CL3)
Linear (CL4)
y = -0.0246x + 2683.9
y = -0.0390x + 3,106.3120
y = -0.0107x + 1637.2
Average Total Phosphorus Concentration, µg/g DW
3000
2500
2000
1500
1000
500
0
1/1/1995
1/1/1999
1/1/2003
1/1/2007
1/1/2011
1/1/2015
1/1/2019

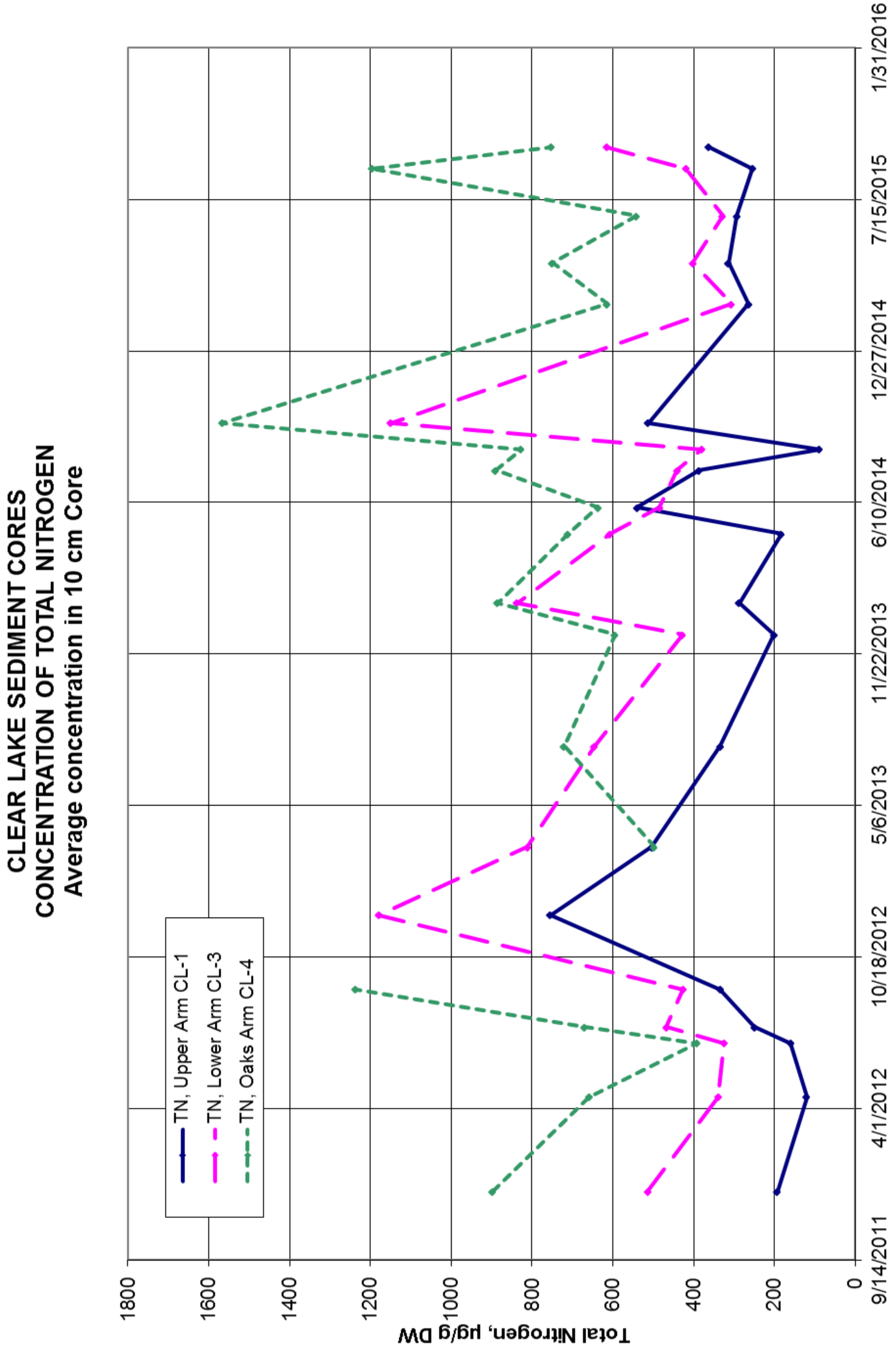

Total Phosphorus
In Top 10 cm of Clear Lake Sediments
Total Phosphorus, metric tons
0
1,000
2,000
3,000
4,000
5,000
6,000
1/1/1995
1/1/1999
1/1/2003
1/1/2007
1/1/2011
1/1/2015
1/1/2019
Lake 10/29/97
TP = -0.1362 x 35732 + 8037
TP = 3,170 T
Lake 9/22/15
TP = -0.1362 x 42269+ 8037
TP = 2,280 T
CL1
CL3
CL4
Lake
Linear (CL1)
Linear (CL3)
Linear (CL4)
Linear (Lake)
y = -0.1362x + 8037.2
y = -0.0963x + 5703.6
y = -0.0273x + 1688.3
y = -0.0127x + 677.64

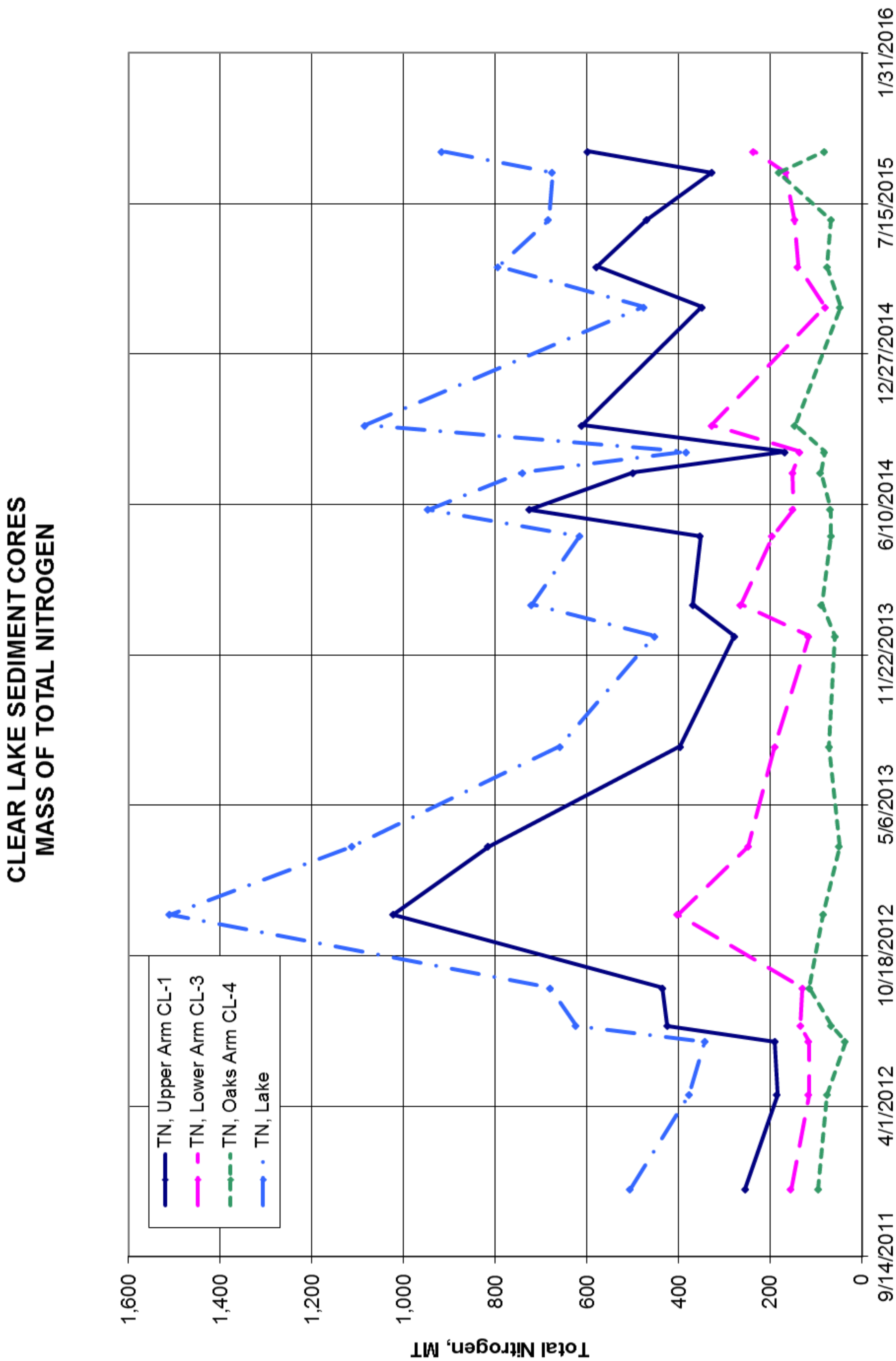

Average Calcium Bound Phosphorus (HCl Extractable) Concentration
In Top 10 cm of Clear Lake Sediments
Average Calcium Bound Phosphorus Concentration, µg/g DW
1600
1400
1200
1000
800
600
400
200
0
1/1/1995
1/1/1999
1/1/2003
1/1/2007
1/1/2011
1/1/2015
1/1/2019
CL1
CL3
CL4
Linear (CL1)
Linear (CL3)
Linear (CL4)
y = 0.0222x - 463.08
y = 0.0108x - 83.776
y = 0.0118x - 135.35


Calcium Bound Phosphorus (HCl Extractable)
In Top 10 cm of Clear Lake Sediments
Calcium Bound Phosphorus, metric tons
0
200
400
600
800
1000
1200
1400
1600
1800
2000
1/1/1995
1/1/1999
1/1/2003
1/1/2007
1/1/2011
1/1/2015
1/1/2019
y = 0.00229x + 608.75399
y = 0.00186x + 440.12673
y = 0.00417x - 16.63989
y = -0.000362x + 52.891556
CL1
CL3
CL4
Lake
Linear (CL1)
Linear (CL3)
Linear (CL4)
Linear (Lake)


Average Iron and Aluminum Bound Phosphorus (NaOH Extractable)
Concentration In Top 10 cm of Clear Lake Sediments
Average Iron and Aluminum Bound Phosphorus Concentration, µg/g DW
1000
900
800
700
600
500
400
300
200
100
0
1/1/1995
1/1/1999
1/1/2003
1/1/2007
1/1/2011
1/1/2015
1/1/2019
CL1
CL3
CL4
Linear (CL1)
Linear (CL3)
Linear (CL4)
y = -0.00725x + 859.81524
y = -0.00695x + 745.08130
y = 0.00225x + 199.40860


Average Iron and Aluminum Bound Phosphorus (NaOH Extractable)
Concentration In Top 10 cm of Clear Lake Sediments
Average Iron and Aluminum Bound Phosphorus Concentration, µg/g DW
0
100
200
300
400
500
600
700
800
900
1000
1/1/1995
1/1/1999
1/1/2003
1/1/2007
1/1/2011
1/1/2015
1/1/2019
CL1
CL3
CL4
Linear (CL1)
Linear (CL3)
Linear (CL4)
y = -0.00725x + 859.81524
y = -0.00695x + 745.08130
y = 0.00225x + 199.40860


CLEAR LAKE SEDIMENT CORES
CONCENTRATION OF TOTAL NITROGEN
Average concentration in 10 cm Core
TN, Upper Arm CL-1
TN, Lower Arm CL-3
TN, Oaks Arm CL-4
Total Nitrogen, µg/g DW
0
200
400
600
800
1000
1200
1400
1600
1800
9/14/2011
4/1/2012
10/18/2012
5/6/2013
11/22/2013
6/10/2014
12/27/2014
7/15/2015
1/31/2016


CLEAR LAKE SEDIMENT CORES
MASS OF TOTAL NITROGEN
TN, Upper Arm CL-1
TN, Lower Arm CL-3
TN, Oaks Arm CL-4
TN, Lake
Total Nitrogen, MT
0
200
400
600
800
1,000
1,200
1,400
1,600
9/14/2011
4/1/2012
10/18/2012
5/6/2013
11/22/2013
6/10/2014
12/27/2014
7/15/2015
1/31/2016